

# Diazotype – A Historical Copying Process

Matthias Ducci\*

Department of Chemistry, University of Education Karlsruhe, Karlsruhe, Germany

\*Corresponding author: [ducci@ph-karlsruhe.de](mailto:ducci@ph-karlsruhe.de)

Received October 11, 2021; Revised November 12, 2021; Accepted November 28, 2021

**Abstract** Diazotype is a historical light tracing process which was used, in particular, for reproducing technical drawings. This paper first explains the principle of the diazotype. Thereafter, a researching and developing teaching concept with a variety of newly developed experiments is presented for chemistry lessons at secondary level II.

**Keywords:** diazonium salt, photolysis, azo dye, fluorescence, diazotype

**Cite This Article:** Matthias Ducci, "Diazotype – A Historical Copying Process." *World Journal of Chemical Education*, vol. 9, no. 4 (2021): 136-143. doi: 10.12691/wjce-9-4-6.

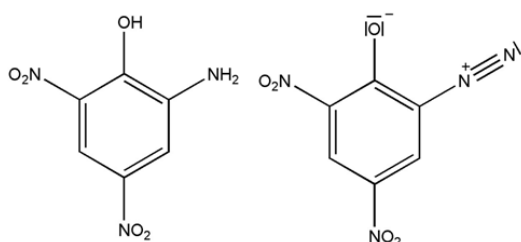
## 1. Introduction

Diazotype is an imaging technique which was used until the 90s of the 20th century for producing copies. From the chemical point of view, this technique is based on the photosensitivity of diazonium cations and the synthesis of azo dyes. The latter are firmly anchored as a topic in most curricula of the upper secondary school level in Germany. Therefore, the diazotype is ideally suited to implement photochemistry content in chemistry lessons.

The following sections describe the discovery of the diazo compounds as well as the historical development of the diazotype. Subsequently, a teaching concept is presented for students to discover the principle of the diazotype and explore it largely independently. Thereafter, this paper addresses variations of the diazotype, which offer many starting points for student research work.

## 2. The Discovery of the Diazo Compounds

The brewing chemist Peter Griess made a groundbreaking observation in 1858: When he poured nitrous acid into picramic acid, a brassy yellow precipitate was formed after some time [1]. This was the first synthesis of a diazo compound. The systematic name of picramic acid is 2-amino-4,6-dinitrophenol. Thus, the resulting precipitate was 2-diazo-4,6-dinitrophenol (cf. Figure 1).



**Figure 1.** Structural formulae of picramic acid (left) and 2-diazo-4,6-dinitrophenol (right)

In the subsequent years, Griess wrote several papers in which he reported on the properties and reactions of this new class of substances. However, the structure of the diazo compounds was unknown to him. Moreover, the assumptions he published on this subject turned out to be wrong [2]. An important contribution to clarify the structure was made by August Kekulé. He started from the assumption that the nitrogen group -N<sub>2</sub> is connected to the carbon skeleton of benzene at only one site [3]. His considerations were confirmed by the successful diazotisation of fivefold substituted aminobenzenes. Kekulé gave the diazonium salts the general formula Ar-N=N-X which, in fact, was already quite close to the present-day notation Ar-N<sup>+</sup>≡N|X<sup>-</sup>.

## 3. The Photosensitivity of Diazo Compounds and Diazonium Salts

The photosensitivity of diazo compounds and diazonium salts was discovered as early as in 1886 [4]. The observation was made that certain compounds, such as 3-diazosalicylic acid, form a coloured product in the light. This fact was made use of already at the end of the 19th century to produce light images with such compounds. However, the underlying chemical processes were elucidated much later by Oskar Süss [5]. As he found out, 1,2-quinonediazides, i.e. compounds also including 3-diazosalicylic acid, undergo a Wolff rearrangement. In this process, nitrogen is split off under the influence of light and a cyclopentadiene derivative is formed under ring contraction. This derivative, in turn, couples with the 1,2-quinonediazide is still present to form the azo dye.

In the subsequent periods, other imaging techniques were developed based on the photosensitivity of diazo compounds, which in their entirety are referred to as diazotype. In 1889, for instance, Albert Feer applied for a patent for a photographic process. His photosensitive mixtures consisted of alkali salts of aromatic diazosulphonic acids (Ar-N=N-SO<sub>3</sub>Na) and phenols or amines. They reacted with each other only in sunlight to form the azo dye. Hence, it can be assumed that free

diazonium ions are formed from the diazosulphonate ions by photolysis [6].

Also, the primuline process is worth mentioning, which goes back to the Englishmen Arthur George Green, Charles Frederick Cross and Edward John Bevan [7]. They prepared tissue and paper with diazotised primulin and similar compounds. Then, they exposed the material through a stencil, converting the diazo compound to phenol in the exposed areas according to  $\text{Ar-N}_2^+ + 2 \text{H}_2\text{O} \rightarrow \text{Ar-OH} + \text{N}_2 + \text{H}_3\text{O}^+$ . Afterwards, the exposed material was developed in alkaline baths containing a coupling component. The major difference to Feer's process was that positives turned into negatives again. This principle was later to become established. However, with primuline Green, Cross and Bevan made a poor choice: the phenols resulting from photolysis produced a yellow background, which was the reason that their process did not attain any commercial significance. In 1894, Momme Andresen detected that all diazo compounds decompose more or less rapidly in the light [8].

In the subsequent decades, Gustav Kögel paved the way with the decisive development steps in the field of diazotype. He mainly used *o*-diazophenols, such as 1-diazo-2-naphthol-4-sulfonic acid. His approach was the same as that of Green, Cross and Bevan, with the exposed images being developed in alkaline solutions with a dissolved coupling component. Later, he discovered that the diazonium and coupling components did not react when tartaric or citric acid was added and prepared the paper with such mixtures. The development was initially carried out in alkaline baths, which he finally replaced with gaseous ammonia. His process was then fully developed. In 1924, the first diazotype paper came onto the market under the name Ozalid M, which was treated with a mixture of 2-diazo-1-naphthol-5-sulfonic acid, phloroglucinol, tartaric acid, a nickel salt and other substances. The Ozalid paper proved to be very successful in commercial terms. Just 6 years after its introduction, the diazotype process accounted for almost 80% of the copies made on the German market.

### 3.1. Mechanistic Considerations

When aromatic diazonium salt solutions are irradiated, nitrogen is split off very easily (dediazotisation) [9]. Basically, photolysis can take place in two different pathways [10]: During the heterolytic cleavage of the C-N bond, aryl cations are formed in addition to elemental nitrogen. They react with nucleophilic partners to form substitution products. This process corresponds to an  $\text{S}_{\text{N}}1$  reaction. The second pathway is a radical process. Here, an electron is transferred from the anion or the solvent to the diazonium group. The resulting aryldiazo radical decomposes to nitrogen and an aryl radical (cf. Figure 2). The latter preferably react with the solvent under H abstraction such that a benzene derivative and a solvent radical are formed. In water, only phenols are formed due to its low reduction effect [10]. Since the diazotype process takes place in aqueous solutions, this pathway is considered in more detail below.

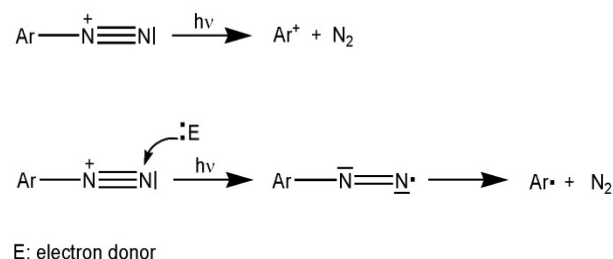


Figure 2. Ionic (top) and radical (bottom) C-N bond cleavage.

The light absorption excites the diazonium cation into a short-lived singlet state. The nitrogen is split off quickly to form the singlet cation. Under certain conditions, triplet states can be assumed from both the singlet diazonium cation and the singlet aryl cation by ISC (intersystem crossing). In this case, the further processes after splitting off nitrogen would be of a radical nature [11]. Starting from the singlet aryl cation (ionic pathway), the next available nucleophile is bound. For statistical reasons, this is a solvent molecule, i.e. a water molecule, which subsequently splits off a proton under phenol formation (cf. Figure 3). However, it cannot be ruled out that also chloride ions are accumulated in a hydrochloric acid solution [9].

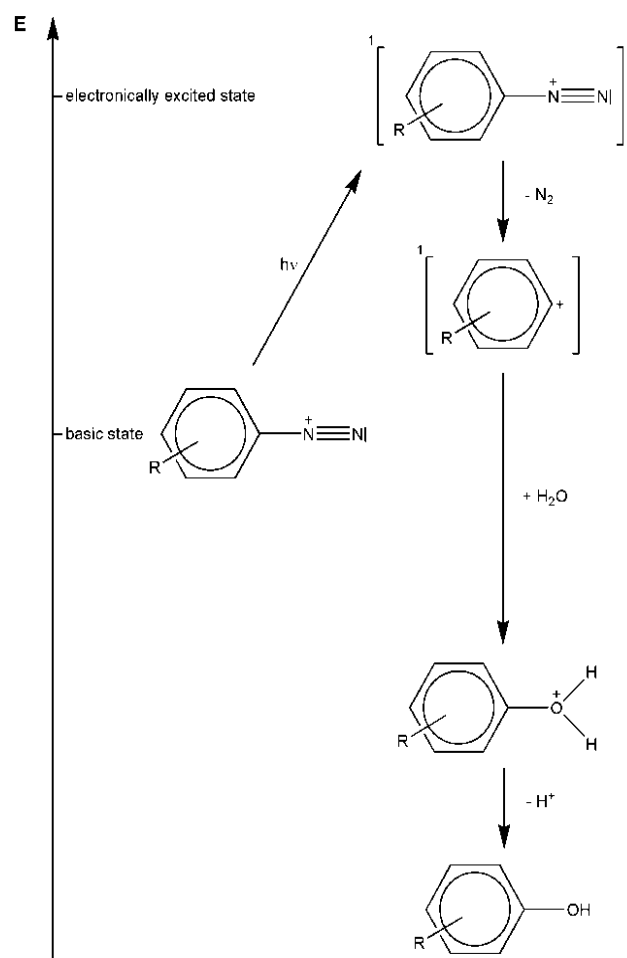


Figure 3. Sequence of photolysis and subsequent phenol formation after ionic decay of the excited singlet diazonium cation (modified according to [11])

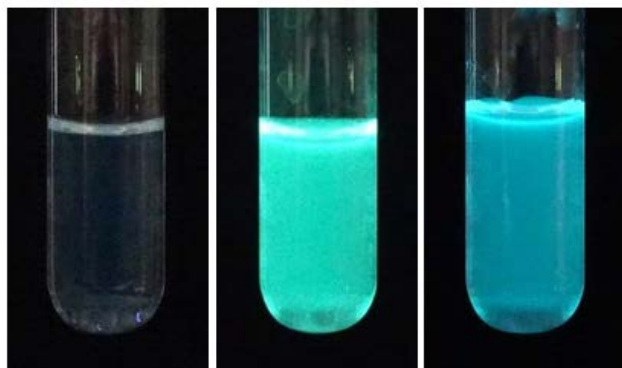
## 4. Diazotype - a Topic for Chemistry Lessons?...!

The topic of azo dyes is - as already mentioned in the introduction - firmly anchored in the educational curricula of most German states. Thus, the diazotype can be readily implemented in chemistry lessons at secondary level II. Moreover, it is a topic which is excellently suited for university teaching as part of a practical course on organic chemistry. Dealing with this process does not only provide deeper insights into the mechanism of azo coupling but is also a very good way to address the content of photochemistry due to the easy-to-understand process of photolysis during exposure. In addition, imaging processes are highly aesthetic and thus have a considerable motivational potential. In addition, this topic offers students the opportunity to be creative, e.g. in making stencils and choosing motifs.

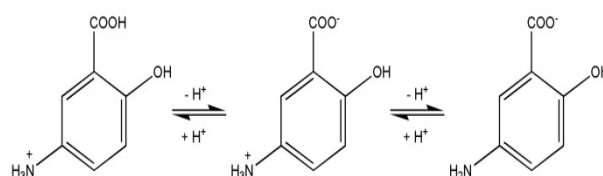
It has proven useful in chemistry lessons to use an exploratory-developmental approach to work on content. Hence, a teaching concept is described below in which the students, on their own, discover the photolysis of diazonium cations and explore the principle of the diazotype. The teacher plays the role of a moderator who steers and drives the learning and cognition process by giving targeted impulses. The author has already published a first suggestion for this [12]. The following extended approach partly follows the historical development of the diazotype.

### 4.1. The Teaching Concept

The learning preconditions of students for implementing this lesson are diazotisation as well as azo coupling. In the beginning students get to know the 5-aminosalicylic acid (5-ASA), an aromatic amine which is used for synthesising an azo dye. When investigating the properties of this substance, the students discover that an aqueous solution of 5-ASA (dissolve a few crystals in 2 mL of tap water) fluoresces mint green under UV light ( $\lambda = 365$  nm). The fluorescence can be extinguished by acidifying with a few drops of hydrochloric acid ( $c = 0.1$  mol/L) and evoked again by subsequently adding sodium hydroxide solution ( $c = 0.1$  mol/L). In the strongly alkaline range, the solution fluoresces blue-green (cf. Figure 4). This behaviour is caused by the shift of equilibria (cf. Figure 5).



**Figure 4.** Acidic (left), neutral (middle) and alkaline 5-ASA solution under UV light ( $\lambda = 365$  nm). (Photographs: Ducci)



**Figure 5.** Equilibria of 5-ASA in aqueous solution

The next teaching section is focussed on diazotisation. To this end, 0.04 g 5-ASA are dissolved in 2.5 mL sodium hydroxide solution ( $c = 2$  mol/L) in a test tube and 0.02 g sodium nitrite (dissolved in 1 mL water) are added. The test tube is placed in an ice bath. Another test tube with 2.5 mL hydrochloric acid ( $c = 4$  mol/L) is also placed there. After the temperature of both solutions has fallen to about  $0$  °C, the alkaline solution is slowly dropped into the hydrochloric acid while stirring. During this step, the temperature in the mixture must not rise above  $5$  °C. The solution is then given a rest in an ice bath for about 30 min. During this time, a solid is precipitated. To examine it, a small amount of the suspension is dried on a filter paper. The solid has a shiny silvery appearance (cf. Figure 6).



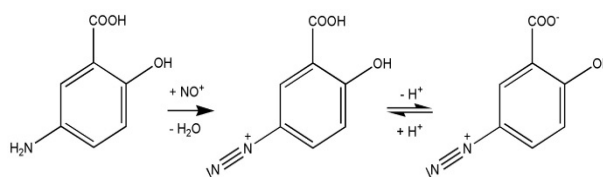
**Figure 6.** 5-Diazosalicylic acid. (Photograph: Ducci)

Obviously, a solid diazo compound has been formed. This assumption can be substantiated by heating a substance sample (about 0.0025 g) with the flame of a lighter: The solid decomposes abruptly with gas release (nitrogen) (cf. Figure 7) and thus reveals its thermal instability, which is typical for diazo compounds.



**Figure 7.** Thermolysis of 5-diazosalicylic acid. The time between the two images was 1/25 s. (Photographs: Ducci)

Figure 8 shows the diazotisation with structural formulae. Precipitation occurs when a proton is split off.

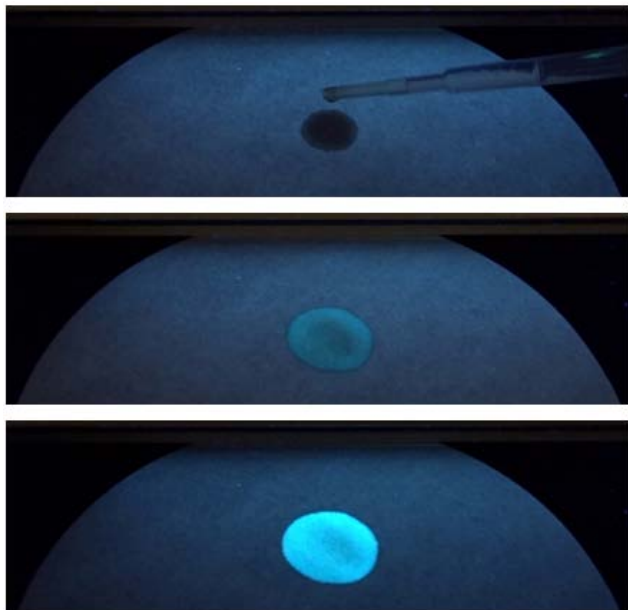


**Figure 8.** Diazotisation of 5-ASA and formation of 5-diazosalicylic acid



However, part of the diazo compound is also present protonated and thus dissolved. This can be demonstrated by mixing a drop of the supernatant solution with a drop of an alkaline phloroglucinol solution (e.g. 0.02 g phloroglucinol dissolved in 2 mL sodium hydroxide solution,  $c = 2 \text{ mol/L}$ ) on the spot plate. The result is a dark red azo dye.

The following experiment reveals another surprising result: A drop of the diazonium salt solution is placed on a filter paper under UV light ( $\lambda = 365 \text{ nm}$ ). Within a few seconds, the initially non-fluorescent solution develops a blue-green fluorescence, which intensifies within a minute (cf. Figure 9).



**Figure 9.** Diazonium salt solution under UV light ( $\lambda = 365 \text{ nm}$ ); top: immediately after dropping the solution onto a filter paper; middle: after 5 seconds; bottom: after 45 seconds). (Photographs: Ducci)

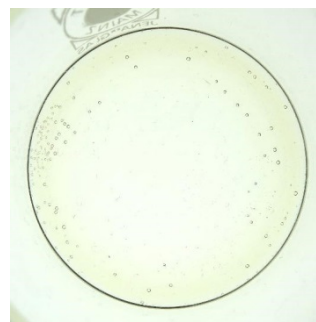


**Figure 10.** Left: Photochemically generated image using a fern leaf under UV light. Right: The same image after prolonged irradiation with UV light ( $\lambda = 365 \text{ nm}$ ). (Photographs: Ducci)

The students attribute this phenomenon either to a photochemical reaction as a result of which a fluorescent product is formed or to the steady drying up of the liquid. Both hypotheses can be easily checked: Another filter paper is wetted with a few drops of the diazonium salt solution. After the filter paper has dried, a stencil (leaf of a plant or similar) is placed on it and exposed to a hand-held

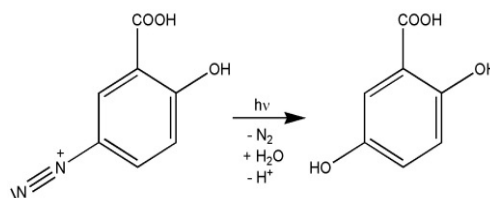
UV lamp for about 1 minute. Then, the stencil is removed and the filter paper is again viewed under UV light. It is clearly visible that the previously covered areas do not fluoresce (cf. Figure 10, left). Thus, the fluorescence can be clearly attributed to the product of a photochemical reaction.

The elucidation of this reaction can be supported by another experiment. UV light irradiation, for instance, of a thin film (height of the liquid about 2 mm) of the diazonium salt solution for five minutes yields the observation that tiny gas bubbles are formed in the liquid (cf. Figure 11).



**Figure 11.** Irradiation of the diazonium salt solution leads to the formation of gas bubbles of nitrogen. (Photograph: Ducci)

From that observation, the students can conclude that a nitrogen molecule is split off from the diazonium cation. The diazonium cation in turn reacts with the next available nucleophile. A water molecule attaches, forming a hydroxyl group under deprotonation (cf. Figure 12). 2,5-dihydroxybenzoic acid is formed which fluoresces under UV light ( $\lambda = 365 \text{ nm}$ ).



**Figure 12.** Illustration of photolytic nitrogen removal with subsequent formation of 2,5-dihydroxybenzoic acid with structural formulae

The students quickly notice that the images generated in this way fade when they are viewed under UV light for a lengthy period of time or frequently since this causes the decay also of the diazonium cations in the previously covered areas (cf. Figure 10, right). This raises the exciting question of how the image can be fixed. The answer is obvious and also given by the students: The diazonium cations in the areas protected from the UV rays must be reacted with a coupling component to form an azo dye. The students know from what they learnt before about the synthesis of azo dyes that an alkaline solution of a suitable reactant partner, such as 2-naphthol, resorcinol or phloroglucinol, is needed to this end. The teacher contributes the additional explanation that filter paper is not a suitable substrate for this process. It is, therefore, recommended to use commercially available light brown or yellowish writing paper, which does not contain optical brighteners.

Procedure: A paper blank, e.g. 5 cm x 5 cm, is coated with the diazonium salt solution using a brush. After the

paper has dried, a stencil is placed on it and the paper is irradiated with UV light for 5 minutes. Then, the paper is dipped in an alkaline phloroglucinol solution (e.g. 1 g phloroglucinol in 50 mL sodium hydroxide solution,  $c = 2$  mol/L) for 5 seconds. The result is a red image of inferior sharpness since the colour runs during wet chemical development or fixation. The students are informed that this procedure is the same as that used in the beginnings of the diazotype. Moreover, they learn that the process was optimised over time. The main improvements were the following:

1. The coupling component is already added and mixed into the diazonium salt solution before the solution is applied to the paper. Early reaction is prevented by adding tartaric or citric acid.

2. The image is fixed with the help of gaseous ammonia instead of caustic soda.

Three solutions are needed for the procedure:

- (i) a diazonium salt solution (preparation see above; to this solution 3 mL hydrochloric acid,  $c = 4$  mol/L are added to dissolve part of the precipitate);

- (ii) a tartaric acid solution (0.25 g tartaric acid dissolved in 2 mL water); and

- (iii) a phloroglucinol solution (0.03 g phloroglucinol dissolved in 2.5 mL sodium hydroxide solution,  $c = 2$  mol/L).

Then, 0.5 mL of the phloroglucinol solution are mixed with 0.5 mL of the tartaric acid solution and stirred well. Only then 1 mL of the diazonium salt solution is added. The mixture is applied as evenly as possible to the substrate (paper blank of about 8 cm x 6 cm) with the help of a bristle brush. After drying, a stencil, e.g. a black and white picture printed on foil, and a glass plate or Petri dish on top are placed on the substrate. It is irradiated with UV light for at least 15 min ( $\lambda = 365$  nm, a hand-held UV lamp should be used and the distance between the paper and the radiation source should not exceed about 0.5 cm). Finally, the paper is transferred into a glass vessel in which the atmosphere is enriched with ammonia gas using concentrated ammonia solution. The result is a reddish-brown image of astonishing sharpness (cf. Figure 13). The coupling reaction taking place is shown in Figure 14 with structural formulae. The fluorescence in the bottom photo of Figure 14 is not only attributable to the 2,5-dihydroxybenzoic acid formed. Also, phloroglucinol, which does not react in these areas, fluoresce blue.



**Figure 13.** From top to bottom: Original photo (Ducci), printout as black and white image on foil, image obtained by diazotype, same image under UV light (motif: East Side Gallery Berlin/Germany)

With 2-naphthol as the coupling component red images are obtained, whereas the images are orange when resorcinol is used. The latter images gradually change their colour to yellow after having been removed from the ammonia chamber. However, the colour change can be reversed again with ammonia. Apparently, a pH-sensitive azo dye is formed by coupling to resorcinol.



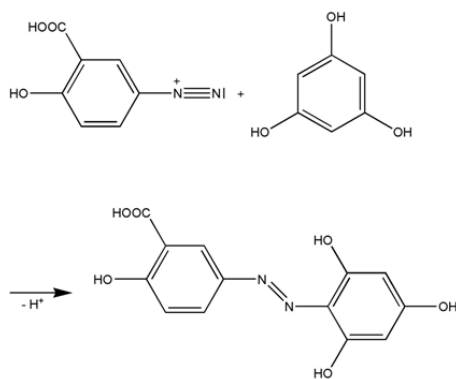


Figure 14. Coupling reaction with phloroglucinol

## 5. Diazo type - Variations

In class, the diazo type can now be tried out with other reactants. This topic is also extremely productive for research work of students in the context of chemistry competitions. For instance, 5-ASA can be replaced by various aromatic amines. 5-Amino-2-methoxybenzoic acid, which is very similar in terms of structure, yields almost identical colours (coupling to 2-naphthol gives a red image (cf. Figure 15, top) and to resorcinol a yellow picture (cf. Figure 16, top)). In the yellow image, many details are best seen under UV light (cf. Figure 16, bottom).



Figure 15. Top: Diazotype with a red azo dye (motif: Temple of Augustus, Pula/Croatia); bottom: Foil print used.



Figure 16. Top: Diazotype with yellow azo dye (motif: Traditional Turkish houses in the centre of Ankara/Turkey); bottom: The same image under UV light ( $\lambda = 365 \text{ nm}$ )

It is also possible during development to create a mixture of azo dyes and thus a resulting mixed colour. The procedure is described in more detail below:

The following solutions are required:

(i) a diazonium salt solution. To prepare it, 0.04 g of 5-amino-2-methoxybenzoic acid is diazotised. The procedure is identical with the diazotisation of 5-ASA. Since no precipitate is formed, there is no need to add hydrochloric acid;

(ii) a tartaric acid solution (0.75 g tartaric acid dissolved in 2 mL water);

(iii) a resorcinol solution (0.03 g resorcinol dissolved in 2.5 mL sodium hydroxide solution,  $c = 2 \text{ mol/L}$ ); and

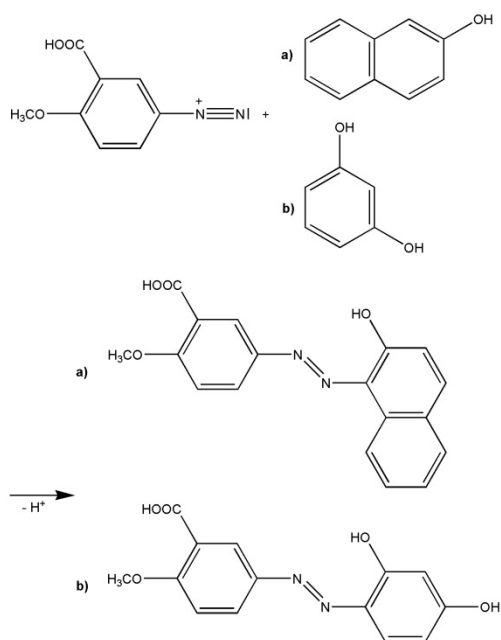
(iv) a 2-naphthol solution (0.03 g 2-naphthol dissolved in 2.5 mL sodium hydroxide solution,  $c = 2 \text{ mol/L}$ ).

For preparing the photosensitive solution, 0.25 mL each of the solutions (iii) and (iv) are mixed and 0.5 mL of the solution (ii) are added. Finally, 1 mL of the solution (i) is added. The mixture is sufficient to prepare two pieces of paper of about 8 cm x 6 cm in size with the help of a brush.

After the paper has dried, a foil with a motif or a stencil as well as a glass plate are placed on it and exposed to UV light ( $\lambda = 365 \text{ nm}$ , use a UV hand lamp, the distance between the paper and the radiation source should not exceed about 0.5 cm) for 15 min. For development or fixation, ammonia is used. The result is shown in Figure 17. The mixture of the red and yellow azo dye produces an orange image. Figure 18 shows the coupling reactions with structural formulae.



**Figure 17.** Diazotype with a mixture of a yellow and a red azo dye (motif: Giant Ferris Wheel in the Vienna Prater/Austria)



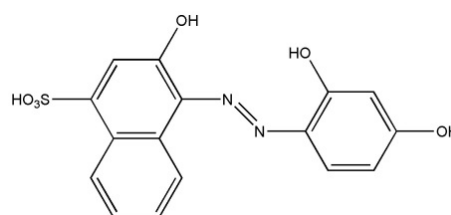
**Figure 18.** Concurrent syntheses ((a) with 2-naphthol and (b) with resorcinol) of a red (a) and a yellow (b) azo dye, yielding the mixed colour orange in Figure 17



**Figure 19.** Diazotype with a blue azo dye (top), which takes on a reddish-brown hue at a lower pH value (outgassing of ammonia) (motif: Kaiser Wilhelm Bridge, Wilhelmshaven/Germany)

As a further amine, 1-amino-2-naphthol-4-sulfonic acid can be used for diazotyping. Coupling to resorcinol yields an initially blue azo dye, which, however, changes to reddish brown within ½ hour (cf. Figure 19).

If the paper is held again in the atmosphere enriched with ammonia, the image takes on the blue colour again. Thus, an indicator effect can be observed also here, which is attributable to the reversible deprotonation of hydroxy groups. The structure of this azo dye is interesting since it contains a 2,2'-dihydroxy-substituted azo compound as a structural element (cf. Figure 20). Such molecules can act as tridentate ligands and form azo complex dyes. Initial experiments using copper(II) ions have already shown that, when complexed, the blue hue remains stable over time.



**Figure 20.** Azo dye with 2,2'-dihydroxy-substituted azo compound

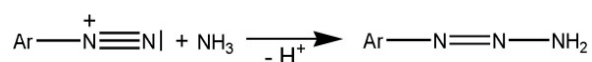
### 5.1. Diazotype “light” Using Ammonia

Finally, a simple variant of imaging is reported, which deviates from the conventional diazotype procedure. This method yields very sharp images and was discovered just by chance during own investigations. 5-Amino-2-methoxybenzoic acid is diazotised and a piece of paper is coated twice with the diazonium salt solution, dried and irradiated with UV light using a stencil. With the help of ammonia (without any further coupling component!), a yellow image is obtained (Figure 21).



**Figure 21.** Diazotype with ammonia under triazene formation (motif: Brandenburg Gate, Berlin/Germany)

Ammonia molecules react with diazosalicylic acid cations to form a yellow diazoamino compound (triazene or aryldiazoamine).



Here, the blue background fluorescence under UV light is exclusively caused by the decomposition product 5-hydroxy-2-methoxybenzoic acid. The formation of triazenes is reversible. They decompose again into their initial components in acid when heated. No coloured reaction products were observed when diazotised 5-ASA or 1-amino-2-naphthol-4-sulfonic acid were used.

## 6. Conclusion

In this article, the development of the diazotype is first briefly explained. Subsequently, new experiments with surprising phenomena are presented and a path of knowledge is proposed, how the interesting topic can be implemented in a researching-developing manner in chemistry classes at different higher-education levels.

## References

- [1] Griess, P., "Vorläufige Notiz über die Einwirkung von salpetriger Säure auf Amidinitro- und Aminotrophenylsäure", *Ann. Chem. Pharm.* 106 (1). 123-125. 1858.
- [2] Griess, P., "Notiz über Diazo-Amidoverbindungen", *Chem. Ber.* 7 (2). 1618-1620. 1874.
- [3] Kekulé, A., *Lehrbuch der Organischen Chemie. Zweiter Band*, Ferdinand Enke, Erlangen, 1866.
- [4] Holzach, K., *Die aromatischen Diazoverbindungen*, Ferdinand Enke, Stuttgart, 1947.
- [5] Süß, O., "Über die Natur der Belichtungsprodukte von Diazoverbindungen. Übergänge von aromatischen 6-Ringen in 5-Ringe", *Ann. Chem.* 556 (1). 65-84. 1944.
- [6] Roth, H. D., "Die Anfänge der Organischen Photochemie", *Angew. Chem.* 101 (9). 1220-1234. 1989.
- [7] Green, A. G., Cross, C. F. and Bevan, E. J., "Ein neues photographisches Verfahren", *Chem. Ber.* 23 (2). 3131-3133. 1890.
- [8] Andresen, M., "Ein neuer Diazotypprozess", *Photograph. Corresp.* 417. 284-288. 1895.
- [9] Wöhrle, D., Tausch, M. W. and Stohrer, W.-D., *Photochemie*, Wiley-VCH, Weinheim, 1998.
- [10] Becker, H. G. O., Ebisch, R., Israel, G., Kroha, G. and Kroha, W., "Kinetik und Mechanismus der Photolyse von Aryldiazoniumsalzen in Methanol", *Journal f. prakt. Chemie.* 319 (1). 98-116. 1977.
- [11] Utterodt, A., *Eignung von Arendiazoniumsalzen als Foto-initiatoren für die kationische Fotopolymerisation*, Dissertation, Halle-Wittenberg, 1999.
- [12] Ducci, M., "Diazotypie – ein bildgebendes Verfahren mit Diazoniumsalzen", *CHEMKON*.

